ON THE RAMAN SPECTRUM OF ALLYL CYANIDE IN THE SOLID STATE*

K. K. DEB AND D. K. MUKHERJEE

OPTICS DEPARTMENT,

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

CALCUTTA-32.

(*Received March*, 15, 1963)

Plate V

ABSTRACT The results of investigation on the Raman spectra of allyl cyanide in the liquid state and in the solid state at −180°C have been discussed. Changes in some of the intramolecular oscillations are found to take place with the solidification of the liquid. It has been concluded from the results that the molecules of the compound are associated through H-atoms and the C ≡ N group when the liquid is solidified and cooled to −180°C.

INTRODUCTION

The Raman spectra of a few organic nitriles in the solid state at −180°C were studied earlier (Bishui, 1948 , Deb, 1961). It was concluded from the results that the lines due to C≡N vibrations in each case undergo changes and a few low-frequency Raman lines appear in the spectra with the solidification of the liquid at low temperatures. In the present work similar investigation has been extended to the case of allyl cyanide.

EXPERIMENTAL

Allyl cyanide supplied by Eastman Kodak Co., U.S.A., was of chemically pure quality and it was further purified by distillation under reduced pressure. The arrangements for recording the Raman spectra in the solid state at −180°C and for studying the state of polarisation of the Raman lines in the liquid state were the same as those used earlier (Deb, 1960 ; Mukherjee, 1960). The spectra were recorded on Ilford Zenith plates with the help of a Fuess glass spectrograph having a dispersion of about 11 Å/mm in the region of 4047 Å.

RESULTS AND DISCUSSION

The Raman spectra of the compound in the liquid state and in the solid state at −180°C are shown in Figs. 1(a) and 1(b), Plate V. The observed Raman shifts of the molecule in the liquid and solid states are tabulated in Table I. The Raman frequencies of the liquid reported by previous workers are also included

*Communicated by Prof. S. C. Sirkar.

in the Table. The states of polarisation of the Raman lines of the liquid are indicated by the letters 'P' and 'D' which mean partially polarised and totally depolarised respectively.

It can be seen from Figs. 1(a), 1(b) and 1(c) and also from Table I that when allyl cyanide is solidified and cooled to $-180°C$, the line 168 cm^{-1} representing probably the bending of C≡N bond appears to be replaced by three new Raman lines of shifts 85, 101 and 187 cm^{-1} respectively. The change may be due to the formation of weak molecular association of different strengths in the crystal lattice at low temperature. Further, in the solid state at $-180°C$ the line 1413 cm^{-1} due to C-H bending oscillation shifts to 1394 cm^{-1} and the line 2257 cm^{-1} due to C≡N stretching oscillation shifts to 2252 cm^{-1}. Also the line 2919 cm^{-1}

TABLE I

Raman spectra of allyl cyanide $\Delta\nu$ in cm^{-1}

Raman shifts Kohlrausch and Stockmeir (1935)		Solid at $-180°C$ Present authors
		85 (5)
		101 (0)
174 (6)	168 (6b) D	187 (3Vb)
205 (4)	212 (1) D	209 (1)
359 (5)	361 (2) D	
404 (5)	407 (2b) P	
	457 (2) P	
555 (2)	558 (0b)	
625 (1)		
864 (5)	866 (6) P	874 (6)
900 (1)		
938 (3)	940 (0)	
1108 (0)		
1221 (4)	1220 (2) P	1220 (2)
1299 (7)	1301 (6) P	1298 (5)
1321 (4)	1322 (2) D	1323 (5)
1410 (7)	1413 (6b) P	1394 (6)
1642 (9)	1645 (10) P	1643 (8)
2245 (-)	2257 (12b) P	2252 (8)
2668 (2)		
2814 ($\frac{1}{2}$)		
2919 (12)	2919 (12b) P	2920 (8)
		2938 (3)
2989 (8)	2990 (4) P	2987 (2)
3030 (8)	3030 (6) P	3027 (6)
3092 (3)	3094 (3) P	3094 (3)

representing the C–H stretching oscillation appears to be split up into two lines 2920 and 2938 cm^{-1} respectively and the intensity of the line 1322 cm^{-1} due to

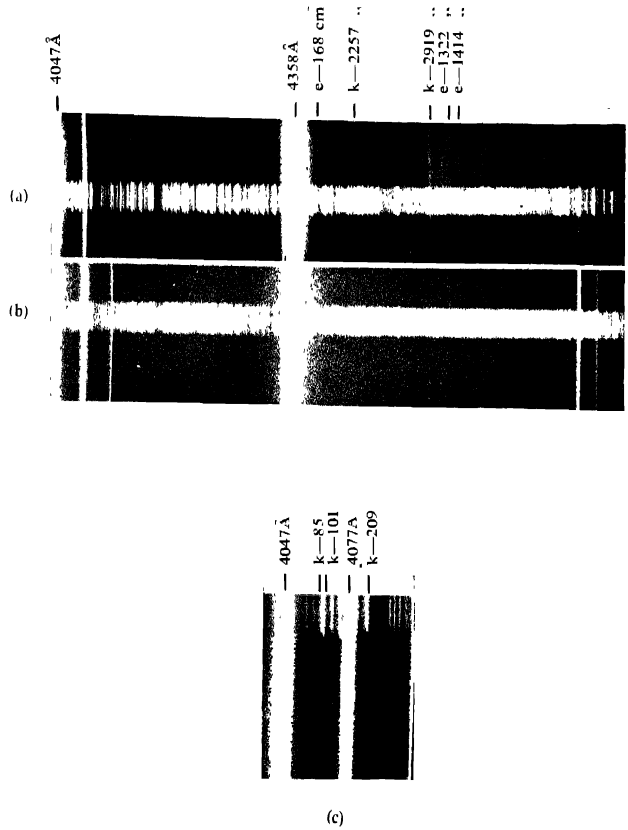

Fig 1. (a) Raman spectrum of allyl cyanide, liquid at 30°C
(b) ,, ,, ,, ,, ,, solid at - 180°C
(c) Low frequency Raman lines of allyl cyanide, solid at —180°C

C-H deformation oscillation increases while that of the line 1301 cm^{-1} remains unaffected when the compound is solidified and cooled to $-180°C$. All the results indicate that the molecules are associated through H-atoms and the C - N group when the liquid is solidified and cooled to $-180°C$. These results agree with those observed in the cases of other nitriles (Bishui, 1948 , Deb, 1961).

ACKNOWLEDGMENT

The authors are highly indebted to Professor S. C. Sirkar, D.Sc , F.N.I., for his kind interest throughout the progress of the work.

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